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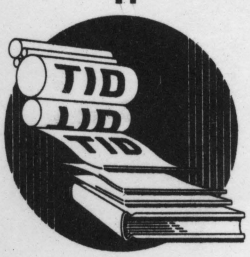

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Abstract

Details are given for simple modifications of a laboratory monochromator so that selected internal standard line pairs from flame spectra may be isolated and measured simultaneously with a multiplier phototube differential photometer. The basic design is applicable to most spectrometers or spectrographs. An atomizing system with provisions for sample recycling and recovery is also described. This equipment has been applied to the determination of calcium in the rare earths in the concentration range of 0.025 to 2.5%. Average deviation for a series of repeated determinations at various concentrations is about ± 1.5%.

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In the application of direct photoelectric methods to the measurement of intensities of flame spectra a new analytical method known as flame photometry has been developed (2). Flame photometric techniques using a monochromator in place of glass and interference filters for spectral isolation have become the preferred method because of the reduction of spectral interference and overall background radiation. The practice with several of the flame photometers of the monochromator type commercially available (1,10) is to measure the spectral line intensity of an element of interest and to compare this with measurements made on standard samples. This technique of measurement does not take advantage of the increased precision and greater freedom from extraneous influences afforded by application of the well known internal standard principle (8). A ratio flame photometer using this principle and its commercial counterpart have been described (3,16) but this instrument is restricted to a single element, lithium, as an internal standard. With a few relatively simple modifications of a laboratory monochromator, it is possible to have an instrument offering the advantages of internal standardization, and in addition, greater flexibility in choosing internal standard lines best suited for various analyses. Furthermore, the need for the more elaborate amplification circuits of the commercial flame photometers is eliminated by the use of multiplier phototubes for measurement of spectral line intensity ratios. The fact that line intensity ratios in flame excitation under controlled conditions do not undergo the continuous changes characteristic of electrical excitation allows the use of simple electrical circuits with suitable band pass to eliminate small, short period fluctuations. Although this instrument is constructed around a commonly available monochromator, the design can readily be extended to any spectrometer or spectrograph.

Description of Internal Standard Flame Photometer

Monochromator. The schematic diagrams in Figures 1 and 2 show the instrument as built around a Gaertner constant deviation monochromator. The burner was positioned to place the tip of the blue cone of the flame about 15 mm. below the optical axis of the spectrometer. Between the burner and the entrance slit of the monochromator, but not shown in the

diagram, is a sliding cover serving the dual purpose of a shutter and to protect the slit jaws from soot from the flame when igniting the acetylene.

In place of the eyepiece or exit slit mechanism normally located at or near the focal plane of the spectrometer, a brass face plate adapter for mounting the exit slits, reflecting mirrors, and photomultiplier tube housing assembly was fitted into the telescope tube. Provisions were also made for rotating the entire assembly to obtain parallel orientation of the slits with the spectral lines.

Flame excitation gives rise to only low temperature lines typical of atoms or molecules in the lowest state of excitation. Consequently, the spectra are very simple. This factor permits a great simplification in the design of the exit slits for measuring line pairs for a variety of analyses. The exit slits were made by first photographing the spectrum of the lines under consideration (Ca 4227 Å and Mn 4031-3-4 Å in the example to be described later) on 2" x 2" squares of Eastman Spectrum Analysis No. 1 plates placed on the telescope tube adapter. These were exposed for 30 seconds with an entrance slit width of 0.1 mm. A positive image was then printed on a square cut from an Eastman 548-G plate. These plates were mounted on the brass face plate as previously indicated.

In attempting to print a positive which had sufficient blackening to exclude all light adjacent to the spectral line, it was found that the lines themselves were exposed slightly with a consequent loss in transmission in the developed image. Therefore the positive print exposures were made to obtain images with as much blackening as possible without definition or transmission losses of the lines and then to paint the adjacent portions of the plate to eliminate the remainder of the overall radiation coming through. For the calcium and manganese lines the linear separation was approximately 3.6 mm. The entire exit slit length of 14.7 mm. was used.

After passage through their respective exit slits the spectral lines were then reflected by first surface mirrors (supplied by Evaporated Metal Films Corporation, Ithaca, New York) to the photocathodes of the high sensitivity 1P21 multiplier phototubes. Since exit slits of this type can be readily made for other spectrometers and spectrographs that may be available, the design is readily adaptable to these instruments.

Atomizer and burner. The air acetylene flame excitation equipment used follows in principle Lundegardh's (13) design, details of which have been reported in the literature (5,14). A few of the modifications which appeared desirable are indicated in the following discussion.

The burner and tip were fabricated of stainless steel. Even though the acetylene pressure could be adjusted to the same gauge reading there were instances in which there was a change in the quantity of acetylene flowing to the burner due to a clogging of the orifice. In addition to the usual manometer for measuring acetylene pressure, a capillary flow-rate meter was inserted in the line from the acetylene tank to the burner. An appreciable change in the gauge pressure for the same flow rate was thus indicative of a partially clogged acetylene orifice.

The all glass atomizer and solution recirculation system is shown in the lower right hand portion of Figure 1. One advantage of such a system is that the burner can be kept in continuous operation without the need for turning off the burner, introducing a new sample into the chamber, and relighting the burner as is done in the usual Lundegardh technique. It is also possible to recycle the solution for readings requiring several minutes or more to complete. Most of the sample can also be recovered with this system. Considerably greater air pressure is required to start the atomizing process when the receiver tube is only partially filled. In manipulating the equipment, the three-way stopcock is turned so the receiver surrounding the capillary can first be completely filled with sample. The solution is then easily drawn up the capillary tube, and when the flow has been started, the stopcock is turned to allow the solution to recycle. After completion of a determination, the sample is drained out of the chamber. The stopcock is then turned so that the receiver tube can be filled with distilled water while at the same time the chamber is being flushed with a fine spray of distilled water from an external line. The washing and draining of the atomizing chamber is repeated three or four times after which the equipment is ready for another determination.

The performance and operation of any given setup of flame excitation equipment is unique in that it is dependent on the particular dimensions of the orifices and other geometry of the apparatus. On the basis of some observations of the behavior of the flame at various air-acetylene combinations, an air pressure of 75 cm. Hg, a capillary flow-rate meter reading of 17.5 cm. water, and an acetylene gauge pressure of 4 cm. water was found to give the most reproducible bridge readings or intensity ratios.

Photomultiplier detector and bridge circuits. Multiplier phototubes are now an accepted measurement device for arc and spark emission analyses (4,9) but their use in flame photometry has been very limited (11,15,18). While this manuscript was in preparation, a commercial flame photometer using photomultiplier tubes was announced(1). The slow acceptance of multiplier phototubes has apparently been caused by several inherent limitations of these tubes, namely, fatigue and large changes in sensitivity with voltage applied to the dynodes. These limitations are readily overcome by use of a bridge circuit and

proper experimental conditions. Compared to conventional phototubes, photomultipliers afford high enough sensitivity to eliminate the need for additional amplification. Thus a photometer can be obtained with a simple circuit involving no more than a battery source, photomultipliers, resistances, and a sensitive null reading device.

The circuit diagram for the photometer is shown in Figure 3. A dynode potential of approximately 100 volts per stage was obtained by setting S_1 to proper voltage as measured with an external voltmeter connected to pinjacks wired from the 8th and 9th dynodes. A Leeds and Northrup Type E galvanometer, catalog No. 2430-D, having a maximum sensitivity of 4×10^{-10} amps. and a period of 3.2 seconds was used both as the null indicating device and, with the shunt control, as a current measuring device. Effects of changes in sensitivity due to fatigue could be avoided, ideally, by having two phototubes perfectly matched with respect to this characteristic, but this is hardly practicable since a large number of tubes are generally not available for matching purposes. Fatigue is dependent on the amount of current drawn (6). Therefore, to minimize this effect, it is advisable to adjust concentrations such that currents greater than 10^{-6} amps. are never exceeded. In cases where tubes having the same fatigue rate are not available, it would be possible to further compensate for differences by subjecting the tube having the lower fatigue rate to a greater current flow, as could be done, for example, by increasing the concentration of the manganese standard. It would also be very feasible to substitute a less expensive 931-A tube for the 1P21 used to measure the manganese photocurrent since sensitivity limitations do not enter in for the internal standard element. Changes in phototube sensitivity due to voltage changes have been found to have been adequately compensated for by use of two tubes in the bridge arrangement as shown. Restandardization can very simply be done by running a reference sample of known concentration at regular intervals as is done in the case of direct photoelectric measurements with arc or spark emission sources.

A series of calcium solutions of known concentration was run to determine the lower limit of detectability with the particular excitation source and photomeasuring device. It was found that concentrations as low as 1.0 ppm. calcium in solution were measurable although the magnitude of the random variations made readings somewhat unreliable. The random variation of the dark current of the particular 1P21 photomultipliers used was found to be less than 1 scale division at maximum galvanometer sensitivity while that of the flame background was 3 to 4 times this deviation. Thus the limiting factor in this instance could be attributed to the latter cause. Much of the unsteadiness in the flame was due to air currents. Under internal standard conditions these fluctuations are "smoothed out" by the bridge circuit. The upper limit of the concentration range is governed by spectral excitation effects and phototube considerations. The 4227 Å line of calcium is

susceptible to reversal and self-adsorption with increasing concentration. For a working concentration range of 5 ppm. to 500 ppm. calcium in solution, currents from 10^{-9} amps. to a maximum of the order of 10^{-7} amps. were drawn through the phototubes.

Bridge manipulations. If a true difference between the IR drop from the current of the test element and internal standard radiations is to be obtained on the bridge, the voltage drop due to the residual current from flame background, general spectral radiation, and random thermionic emission of the tubes must be compensated for by putting a counter e.m.f. across each arm of the bridge. This procedure is described below.

A solution of the matrix, free of the element to be determined, is introduced into the atomizing system. Selector switch S_2 is set to position 1 with the bridge on-off switch S_4 in the off position. Then the appropriate compensator dial is adjusted to give a zero current reading on the galvanometer at maximum sensitivity. This same procedure is repeated when S_2 is in position 2, after which the selector switch is set to the B position and S_4 is turned to the on position. If a null reading is obtained on the galvanometer irrespective of the position of the helixical 20K precision slide wire resistance (Micropot manufactured by Gibbs Division, Borg Corp., Delevan, Wisc.) the IR drop across each arm of the bridge is zero and the compensators have been properly adjusted.

The Micropot was wired so that readings on the Duodial scale (made by Beckman Instruments, Inc., South Pasadena, California) go from 1000 to 0 for the condition $I_{PA} > I_{PB}$ to $I_{PA} = I_{PB}$, where I_{PA} and I_{PB} are, respectively, the net photocurrents on the multipliers picking up radiations from elements A and B. Thus for this condition the bridge reversing switch must be in such a position that the photocurrent of A goes through the Micropot arm of the bridge if a null reading is to be obtained. When $I_{PB} > I_{PA}$, S_3 must be reversed and dial readings go from zero for $I_{PB} = I_{PA}$ toward 1000 as I_{PB} becomes increasingly greater than I_{PA}.

Calculations. Bridge readings with the arrangement of the circuit and Duodial as described above do not give photocurrent ratios directly. To obtain a relationship between these readings and photocurrent ratios, the factor (1000-R)/(1000) for the case where $I_{PA} > I_{PB}$ and (1000)/(1000-R) for $I_{PB} > I_{PA}$ was applied. Since photomultipliers respond linearly to changes in light, intensity ratios are equivalent to current ratios. Following the usual practice in spectrographic analysis, the log of intensity ratio as represented by (1000-R)/(1000) or (1000)/(1000-R) can then be plotted as a function of the log of the concentration.

Analytical Procedure For Determination of Calcium in Rare Earths

Preparation of standards. Solutions of the rare earths were prepared by dissolving the oxides equivalent to 0.500 gms. of the metal in a minimum of calcium-free hydrochloric acid, evaporating to crystals of the chloride, and redissolving the crystals in a few ml. of redistilled water. Standard solutions of calcium were then added to provide calcium to rare earth percentages ranging from 0.025 to 2.5. Constant amounts of a standard solution of manganese were added so that upon dilution of the combined rare earth, calcium, and manganese solutions to 25 ml., the manganese concentration was 0.03%. This provided a 2% solution of the matrix rare earth. The standard calcium solution (2mg/ml.) was made by dissolving double distilled calcium metal in dilute calcium-free hydrochloric acid. The standard manganese solution (1 mg/ml.) was similarly prepared from electrolytic metal. The calcium-free hydrochloric acid was prepared by passing hydrogen chloride gas through double distilled water in a quartz container.

Results

The calibration curve for the determination of calcium in lanthanum is shown in Figure 4. Similar calibration curves for determining calcium in samarium, neodymium, cerium, and praseodymium showed slight but significant shifts in the intercepts as compared to lanthanum. By measuring this difference, a single curve could be used for measuring calcium in the rare earths mentioned.

Although no extensive studies have been made on the precision of measurements, preliminary results indicate a mean deviation of about ± 1.5%. Much of this variation may be attributed to results obtained at the lowest concentration. The results in Table 1 summarize calibration data obtained on three different runs.

Acknowledgement

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Table 1

Reproducibility Data

% Conc. Calcium in Lanthanum	Bridge Readings*			
	3/28/50	3/30/50	4/5/50	Mean
0.025	0.066	0.054	0.060	0.060
0.050	0.106	0.102	0.109	0.104
0.125	0.259	0.260	0.256	0.258
0.250	0.495	0.500	0.504	0.500
0.375	0.727	0.708	0.734	0.723
0.625	1.16	1.14	1.15	1.15
1.25	2.18	2.17	2.17	2.17
2.50	3.73	3.68	3.67	3.69

* From the factor (1000-R)/(1000) or (1000)/(1000-R).

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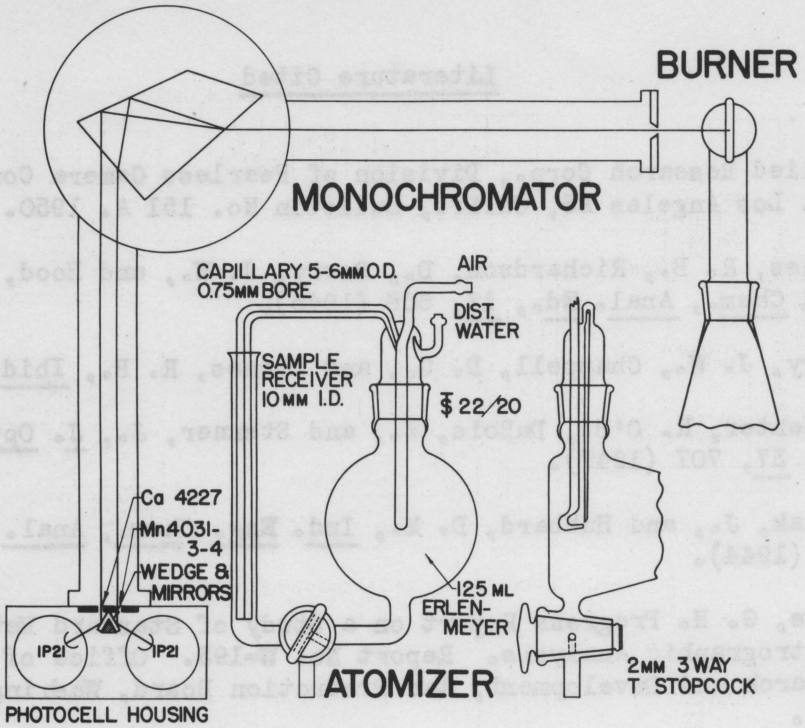

Fig. 1—Monochromator Adaptations and Recycling Atomizer Assembly.

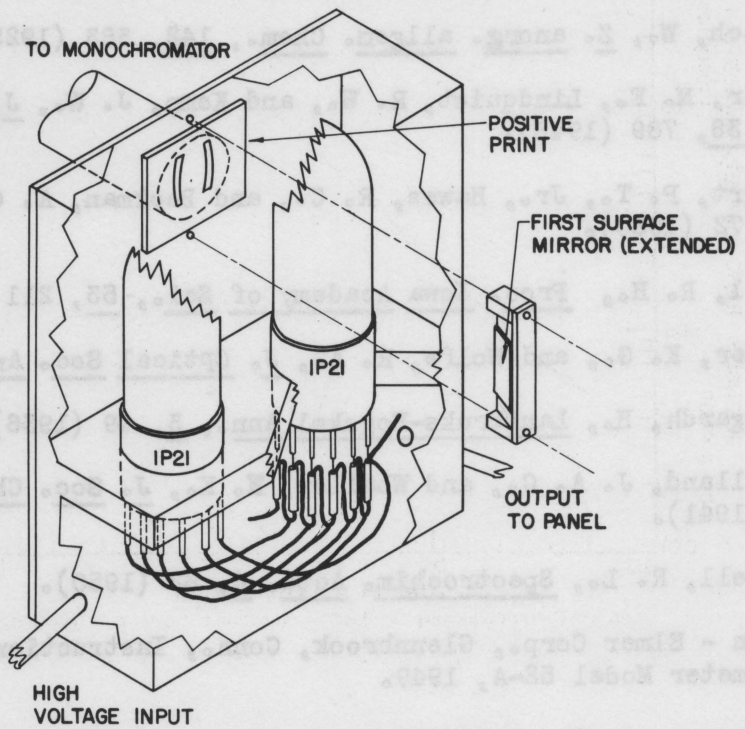

Fig. 2—Cutaway View of Slits and Reflecting Mirrors in Photocell Housing.

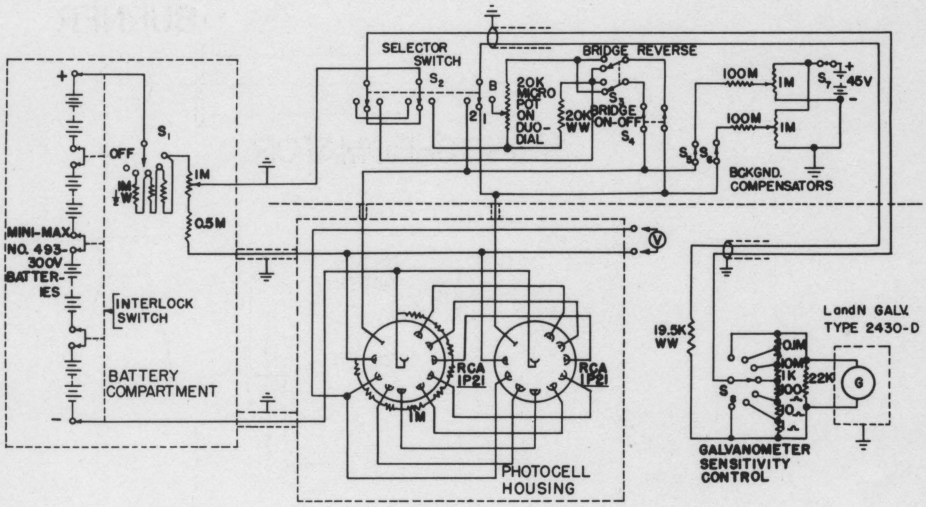

Fig. 3—Circuit Diagram of Internal Standard Flame Photometer.

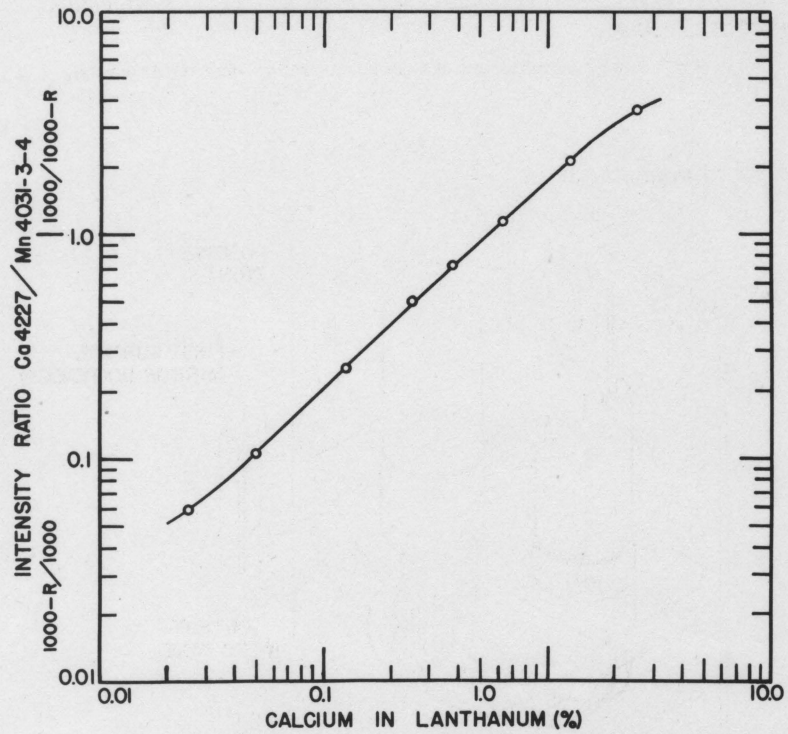

Fig. 4—Calibration curve for the Determination of Calcium in Lanthanum.

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